



## Structural study of the coating effect on the thermal stability of charged MgO-coated $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes investigated by in situ XRD

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### H I G H L I G H T S

- Thermal decomposition reaction mechanism of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and MgO-coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ .
- The decomposition accelerated by the interaction between electrode surface and electrolyte.
- The electrolyte induced thermal decomposition suppressed by MgO surface coating

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### A B S T R A C T

Safety concerns in high-performance lithium rechargeable batteries are one of the major technical barriers that have to be overcome for successful commercialization of more demanding applications like electric vehicles and electric energy storage for renewable energy sources. The thermal stability of the charged cathode materials is critical in the safety characteristics of Li batteries, which is related to the occurrence of exothermic reactions in charged batteries at elevated temperatures that ultimately result in thermal runaway and catastrophic failure of the battery. The thermal runaway has been attributed to the reactions between the charged electrodes and the electrolyte. Therefore, in-depth understanding of the structural changes of the charged cathode material during thermal decomposition reactions, with or without the presence of electrolytes and their relationship with the thermal stability of the cathode material is very important. One of the effective ways to improve the thermal stability of charged cathodes is to modify the electrode materials' surface by coating with stable metal oxides. Here we report the effect of surface modification on the structural changes and their relationship with thermal stability of charged MgO-coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathodes by using in situ XRD technique in a wide temperature range from 25 °C to 450 °C with and without the presence of electrolyte in comparison with bare  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathodes.

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## 1. Introduction

The advent of Li-ion batteries have played a central role in success in portable digital and wireless technology over the past two decades moving into even larger impact on society, for example, in heavy-duty applications such as electric vehicles and energy backup for renewable energy sources. Safety concerns in high-performance lithium rechargeable batteries are one of the

major technical barriers that have to be overcome for more demanding applications like electric and hybrid electric vehicles (EV and HEV). Safety characteristics are related to the occurrence of exothermic reactions in charged batteries at elevated temperatures that ultimately results in thermal runaway and catastrophic failure of the battery [1–4]. The thermal runaway has been attributed to the reactions between the charged electrodes and the electrolyte.

Among efforts to improve the thermal stability of charged cells, one is to modify the electrode material surface by coating with stable metal oxides [5,6]. Since the thermal decomposition of the electrode is through the reaction with the electrolyte at elevated temperatures, proper insulation between the charged electrode

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materials and the electrolyte by the surface coating should be helpful in suppressing the negative impact of the electrolyte during the thermal decomposition reactions. Temperature-dependent X-ray diffraction studies have provided useful information about these reactions. However, most of the previous temperature dependent diffraction studies of the structure of the charged electrodes were carried out in the absence of electrolyte/solvents [7–11], which is not fully representative to the thermal runaway conditions. In order to understand the actual thermal degradation of the electrodes in real Li-ion cells, it is crucial to monitor the structural changes of the charged cathode material in the presence of electrolyte. We have developed a technique using the combination of a high intensity synchrotron X-ray beam and a fast image plate detector to do in situ X-ray diffraction during the thermal decomposition of charged cathode materials in the presence of electrolyte and showed that the negative impact of electrolyte are quite dramatic in the thermal decomposition of the charged electrode in our earlier publications [12–15].

In an effort to further understand the oxide coating effect on the structural changes of the coated and uncoated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and the thermal decomposition mechanism of the charged electrodes, we have thoroughly investigated the structural changes of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  in comparison with the MgO-coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte by using in situ XRD technique. The decomposition path and the structural changes at various state of charge in the presence of electrolyte are presented. The thermal degradation mechanisms of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and MgO-modified  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte are established. This thermal structure study gives a better understanding of the thermal degradation mechanism of nickel-based layered cathode materials at various state of charge in the presence of electrolyte, as well as the effects of MgO surface coating on the cathode materials.

## 2. Experimental

The spherical nickel cobalt hydroxide made by co-precipitation method was used to synthesize  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powders with the particle size of about 10  $\mu\text{m}$ . The magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) solution was used to coat MgO on the surface of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powders. The detailed synthesis procedure and the electrochemical properties of uncoated and MgO-coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powders have been described in the previous report [16]. Cathode specimens were prepared by mixing uncoated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  or MgO-coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powders with 10 wt.% mixture of acetylene black and graphite and 10 wt.% PVDF (poly-vinylidene fluoride) in NMP (*N*-methyl pyrrolidone) solution. The cathodes were incorporated into cells with a Li foil anode, a Celgard separator, and a 1 M  $\text{LiPF}_6$  electrolyte in a 1:1 EC: DMC solvent (LP 30 from EM Industries, Inc.). The cells were assembled in an argon-filled glove box and were hermetically sealed in a housing that could be easily disassembled. The cells were cycled to various states of charge, outside the glove box. The cells were then transferred to the glove box for disassembly and the charged cathode materials were scratched from the current collector and loaded into quartz capillaries in glove box. Some of the charged cathode samples were washed in THF in the glove box to remove the electrolyte before sealing in either 0.3 mm or 0.5 mm quartz capillaries. Other samples were not washed before loading the capillaries and wetted with a drop of excess electrolyte before sealing. In order to simulate the real operating condition, excess electrolyte was added to the capillary to compensate the lost electrolyte during the disassembling of the cell. The capillaries were mounted in the thermal stage of diffractometers on beamline X7B, at National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), and XRD spectra

were recorded as a set of circles on a Mar 345-image plate detector in the transmission mode. A complete XRD spectrum was taken on the image plate within  $\sim 1$  min exposure time and the image plate was scanned and the spectral information transferred to a computer in  $\sim 1.5$  min. Thus the total recording time for a spectrum is  $\sim 2.5$  min.

## 3. Results and discussion

Fig. 1 shows in situ XRD patterns for low charged state cathode  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  (low state of charge at  $\sim 50\%$  SOC) in the absence of electrolyte as a function of temperature. At the room temperature, all diffraction lines can be indexed using a hexagonal axes option of the rhombohedral R-3m space group. The XRD pattern for  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  indicates a well-developed layered structure

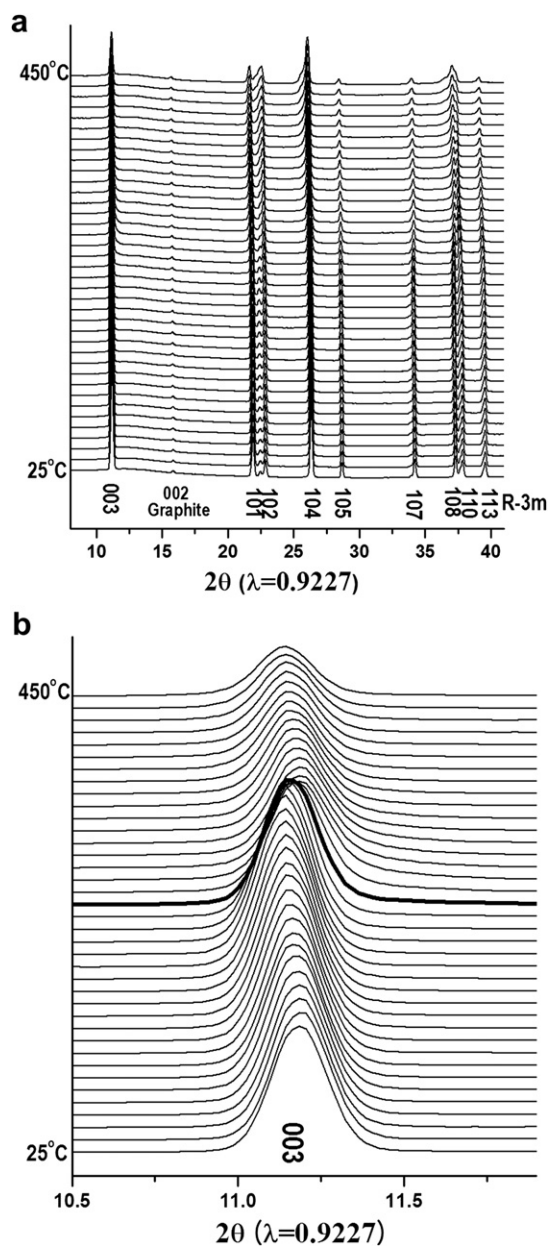
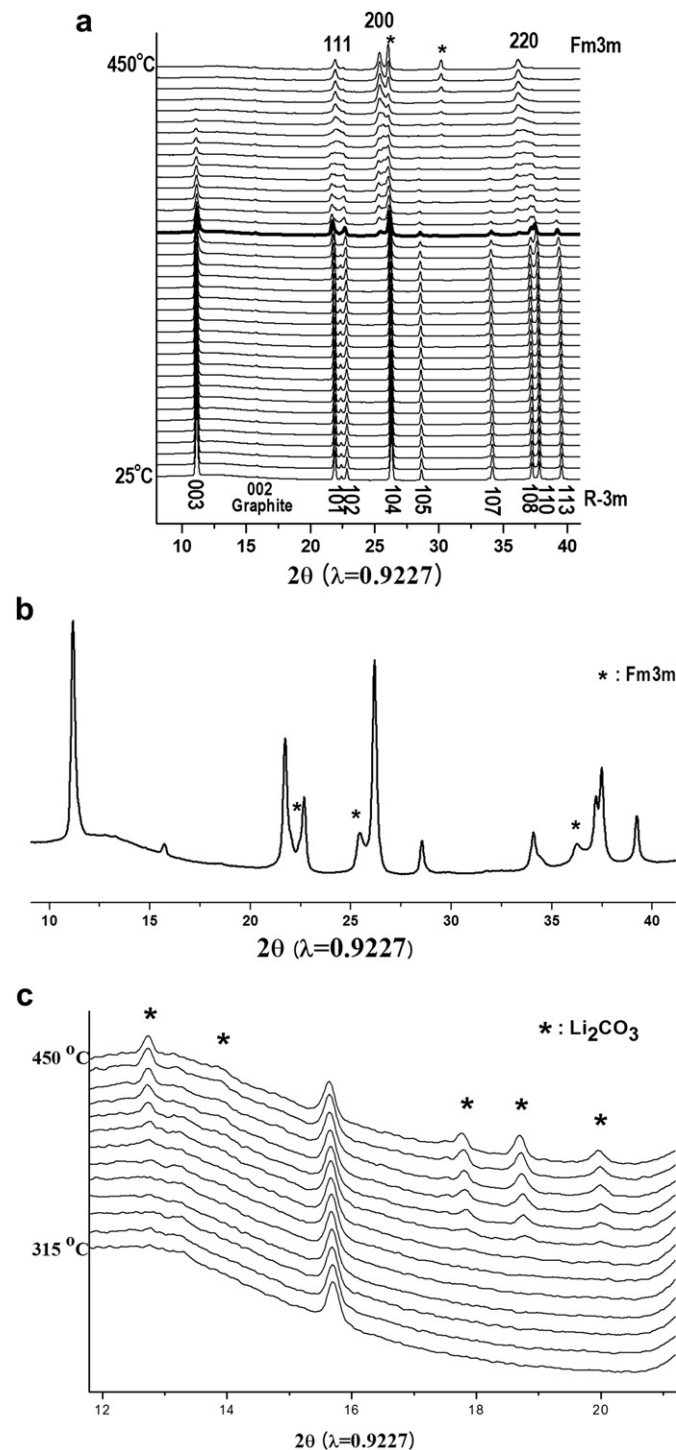


Fig. 1. (a) Time-resolved XRD patterns for  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the absence of electrolyte as a function of temperature. (b) Magnified 003 peaks for (a). Structural change starts at  $\sim 260^\circ\text{C}$  (thick line).

showing the good separations of the (006)/(012) and the (108)/(110) diffraction lines. No structural changes are seen until about 260 °C. As shown in Fig. 1b, the intensity of the critical (003) peak remains unchanged until about 260 °C indicating Ni atoms are not displaced to the Li-atoms planes. The structure of  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the absence of electrolyte still maintains the basic structure of layered phase (R-3m) even at temperature as high as 450 °C, similar as other nickel-based cathode materials at low charged states [12,14]. Fig. 2 shows the XRD patterns for the same sample heated under the same condition but in the presence of electrolyte. It is interesting to note that the presence of electrolyte significantly accelerates thermal decomposition of the charged cathode material. The presence of the electrolyte alters the paths of the structural changes and lowers the temperatures for onset of the reactions comparing with those in the absence of electrolytes [3,12]. Regarding the paths of the structural changes, we can compare it with the thermal decomposition of  $\text{Li}_{1-x}\text{NiO}_2$  type materials in the absence of electrolytes, where the structural changes follow a typical path: the layer structured  $\text{Li}_{1-x}\text{NiO}_2$  converts to a disordered spinel structure ( $\text{LiNi}_2\text{O}_4$ ) first, then the disordered spinel structure converts to a NiO-like rock salt structure [7,8,17]. These decomposition processes involve oxygen release with exothermic reactions that are responsible for the potential dangers of thermal runaway or explosion. In the XRD patterns for  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the absence of electrolyte in Fig. 1, it is somewhat expected that we do not see clear evidence for the spinel phase in the temperature range up to 450 °C, due to the low state of charge ( $x$  value is far from 0.5 and the system is quite stable against thermal decomposition). In contrast, the structural changes of  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte observed in Fig. 2 show quite different path. First of all, the whole sample converted to the rock salt-structured NiO at the end of heating at 450 °C (Fig. 2a) and the signature of its formation was observed at temperature as low as 280 °C (Fig. 2b). Second, the formation of  $\text{Li}_2\text{CO}_3$  is observed in Fig. 2c. This suggests that at low states of charge ( $x < 0.5$ ),  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  reacts with the electrolyte at elevated temperature to form NiO and  $\text{Li}_2\text{CO}_3$ . The formation of  $\text{Li}_2\text{CO}_3$  gives us an important hint of the reaction between the cathode and the electrolyte, which facilitates the conversion to NiO structure in  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  (low state of charge) at temperature as low as 280 °C. In the presence of electrolyte the solvent may act as a reducing agent [4] and the surface lithium extracted from the bulk structure reacts with the solvent, resulting in the formation of  $\text{Li}_2\text{CO}_3$ . This process would consume lithium at the surface of the cathode, accelerate the diffusion of the lithium from the core to the surface, and increase the average oxidation state of nickel cations to the unstable state of higher than  $\text{Ni}^{3+}$  levels. This is equivalent to charging the cathode to a higher charge state, which has been determined to be less stable and cause thermal decomposition at a lower temperature [12]. The rigorous thermal decomposition reaction accelerated by the electrolyte converts the layered structure to the NiO with rock salt structure directly without the formation of spinel phase as an intermediate phase. Therefore, the formation of the  $\text{Li}_2\text{CO}_3$  and the extraction of lithium from the cathode may be the key factor in understanding the acceleration effects of the electrolyte on the thermal decomposition process for the cathode with low state of charge.

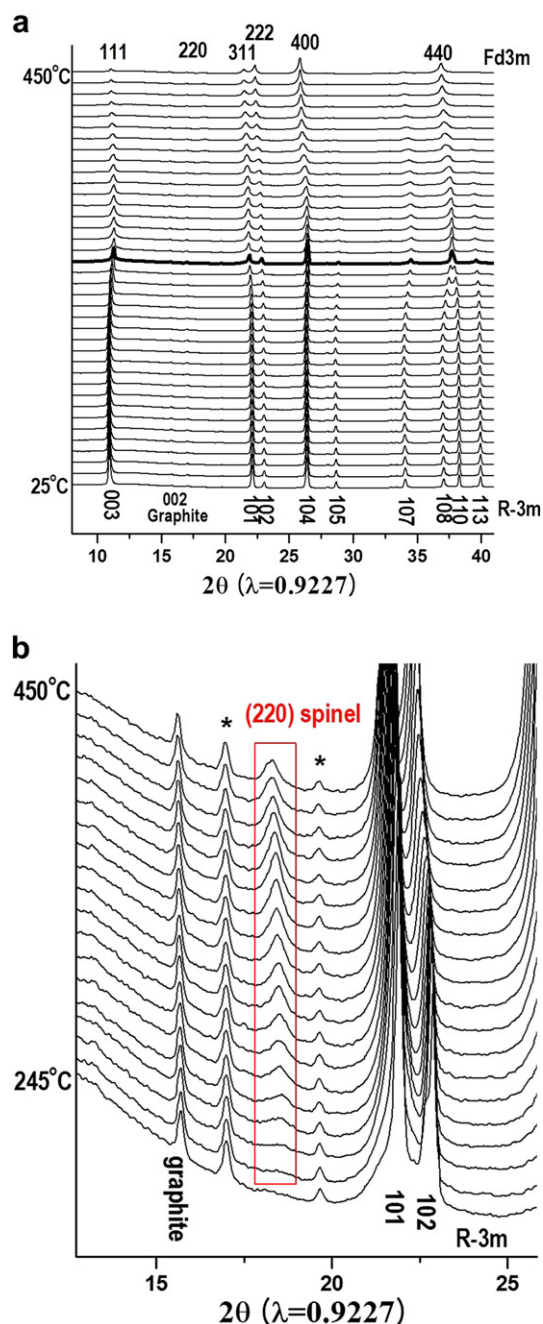
In situ XRD patterns for  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  (high state of charge at ~100% SOC) in the absence of electrolyte are shown in Fig. 3, when heated from 25 to 450 °C. The typical path of structural changes mentioned before can be seen. In the interval between 240 and 280 °C the coalescence of the (108) and (110) peaks in the layered structure is observed suggesting the formation of disordered spinel phase. Based on a  $2 \times 2 \times 2$  cubic rock salt lattice, this merged peak corresponds to the (440) peak in the cubic structure with space group  $\text{Fd}3\text{m}$  [18,19]. As shown in Fig. 3b, The evolution of the (220)

diffraction line also confirms the formation of the spinel phase [9]. At above 260 °C, a cubic structure is observed, consistent with the formation of  $\text{LiNi}_2\text{O}_4$ -like phase. The disordered spinel phase remains mostly unchanged until 450 °C. The formation of the



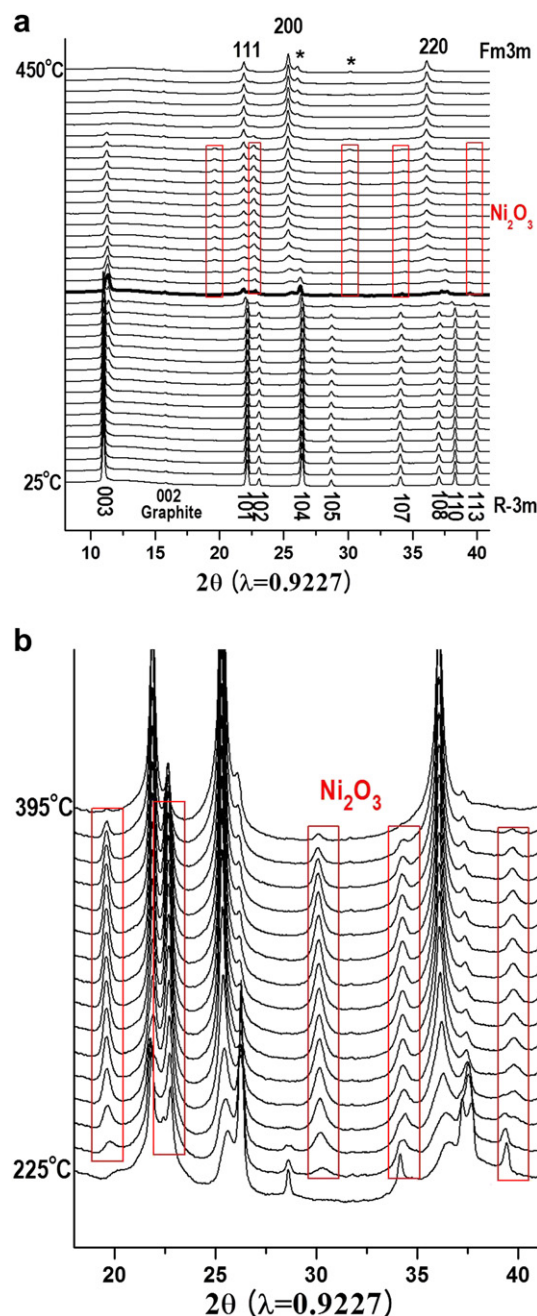
**Fig. 2.** (a) Time-resolved XRD patterns for  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte as a function of temperature. Formation of NiO-like phase starts at ~280 °C (thick line). Asterisk shows formation of metallic nickel phase. (b) Time-resolved XRD pattern for  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  at 280 °C. This is an expanded view of the thick line in (a). Asterisk indicates formation of NiO-like phase ( $\text{Fm}3\text{m}$ ). (c) Magnified XRD patterns in the temperature range between 315 and 450 °C in (a). Asterisk shows formation of  $\text{Li}_2\text{CO}_3$  phase.





**Fig. 3.** (a) Time-resolved XRD patterns for  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the absence of electrolyte as a function of temperature. Formation of spinel phase starts at  $\sim 260^\circ\text{C}$  (thick line). (b) Magnified XRD patterns in the temperature range between  $245^\circ\text{C}$  and  $450^\circ\text{C}$  in (a). Asterisk shows peaks from the heating cell.

disordered spinel with high oxidation state (above  $\text{Ni}^{3.5+}$ ) of nickel delays transformation to more reduced phase like NiO ( $\text{Ni}^{2+}$ ), which could release oxygen violently and may act as a trigger for the thermal runaway. Fig. 4 shows in situ XRD patterns for  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte as a function of temperature. Similar like those observed in Fig. 2 for low states of charge ( $x < 0.5$ ) in  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ , the spectra in Fig. 4 show that the reaction of highly charged cathode with the electrolyte lowers the onset temperature of thermal decomposition and alters the paths of the structural changes compared to that of the same sample without the electrolyte. For this high state of charge sample, the formation of NiO-like phase starts at as low as  $\sim 225^\circ\text{C}$  which



**Fig. 4.** (a) Time-resolved XRD patterns for  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte as a function of temperature. Formation of NiO-like phase starts at  $\sim 225^\circ\text{C}$  (thick line). Asterisk shows formation of metallic nickel phase. (b) Magnified XRD patterns in the temperature range between  $225^\circ\text{C}$  and  $395^\circ\text{C}$  in (a). Empty rectangular shows formation of hexagonal  $\text{Ni}_2\text{O}_3$  phase.

is much lower temperature than the formation of the disordered spinel in the same sample without electrolyte.

Helped by the high sensitivity and fast data collection rate using the synchrotron-based X-ray source and image plate detector, we were able to observe a new structure related to the reduction of  $\text{Ni}^{4+}$  and oxygen release process for the nickel-based cathode materials. In our earlier publication, we reported this intermediate phase in the similar nickel-based cathodes [13]. Although it was not possible to conduct the structural refinement of this phase by the Rietveld method because of the large broadening of the diffraction lines and the presence of coexisting phases, the intermediate phase

could be unambiguously indexed to a  $\text{Ni}_2\text{O}_3$ -like phase with a hexagonal cell. In the expanded XRD patterns shown in Fig. 4b, the Bragg reflections marked by rectangular represent an intermediate  $\text{Ni}_2\text{O}_3$  structure. The phase transitions from the layered structure to the  $\text{Ni}_2\text{O}_3$  and  $\text{NiO}$  start at almost the same temperature, accompanied with the reduction of  $\text{Ni}^{4+}$  to  $\text{Ni}^{3+}$  and  $\text{Ni}^{2+}$  respectively. The structural and Ni-O bond length changes accompanied with the Ni cation reduction (from  $\text{Ni}^{4+}$  in the layered structure to the  $\text{Ni}^{2+}$  in rock salt type  $\text{NiO}$ ) are quite large, which can be seen in the two-theta angle shifts between the corresponding Bragg reflections ( $hkl$ ) in  $\text{Fm}\bar{3}m$  rock salt structure vs  $2x(hkl)$  in spinel  $\text{Fd}\bar{3}m$  structure). The formation of the intermediate structure  $\text{Ni}_2\text{O}_3$  with  $\text{Ni}^{3+}$  serves as a bridge in the large gap between  $\text{Ni}^{4+}$  and  $\text{Ni}^{2+}$ . The formation of the  $\text{Ni}_2\text{O}_3$  structure plays an important role in initiating and assisting the phase transition from layered structure to rock salt type  $\text{NiO}$  structure. Because the amount of this  $\text{Ni}_2\text{O}_3$  structure is very small as the percentage of the total sample and it forms only in part of the heating process and disappears before the end of heating, it has been quite difficult to identify this intermediate phase. Thanks to the high sensitivity and fast rate data collection detector, the image plate, together with the high intensity X-ray source from the synchrotron beamline, we were able to observe the formation of this structure and index it to the hexagonal structured  $\text{Ni}_2\text{O}_3$  phase. As shown in Fig. 4b, the formation and disappearance of  $\text{Ni}_2\text{O}_3$ -like phase is clearly observed in the temperature range between 225 and 395 °C.

The structural changes we have discussed for the uncoated  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  at different state of charge in the absence and presence of electrolytes are quite similar to what we have reported in our previous publications about  $\text{Li}_{1-x}\text{NiO}_2$ ,  $\text{Li}_{1-x}\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , and  $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  systems [12–14]. This gives us the confidence that the results discussed below will be quite helpful in understanding the mechanism of enhanced thermal stability by surface coating to other nickel-based cathode materials, which is not restricted to the  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  system only.

It is well known that the surface modification of oxide cathode materials can improve the performances of the electrode in capacity and cyclability [20–25]. However, not much attention has been paid to the effects of surface coating on the improvement of thermal stability of the cathode materials. Fig. 5 shows in situ XRD

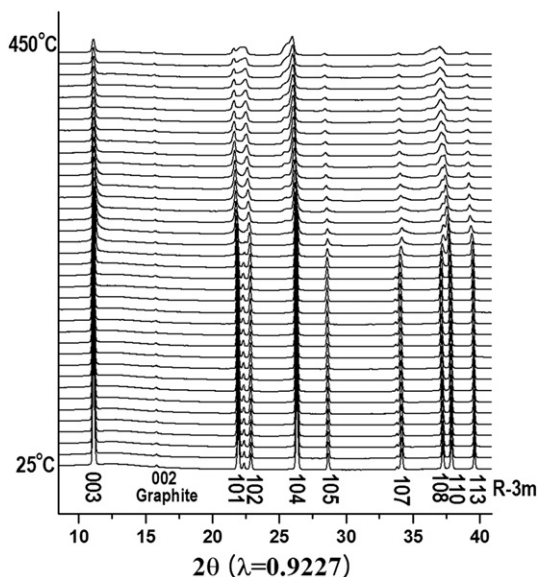


Fig. 5. Time-resolved XRD patterns for MgO-coated  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte as a function of temperature.

patterns for MgO-coated  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte as a function of temperature. Compared to the XRD patterns for uncoated  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte in Fig. 2, the  $\text{Li}_2\text{CO}_3$  and  $\text{NiO}$  structures are not observed in Fig. 5 in the whole heating range up to 450 °C. This is the clear evidence of the thermal suppression effect of MgO coating in the presence of electrolyte showing the improved thermal stability of the charged electrode (low state of charge) at elevated temperatures. Considering the effects on accelerating thermal decomposition of the charged electrode by the presence of electrolyte, it should be noted

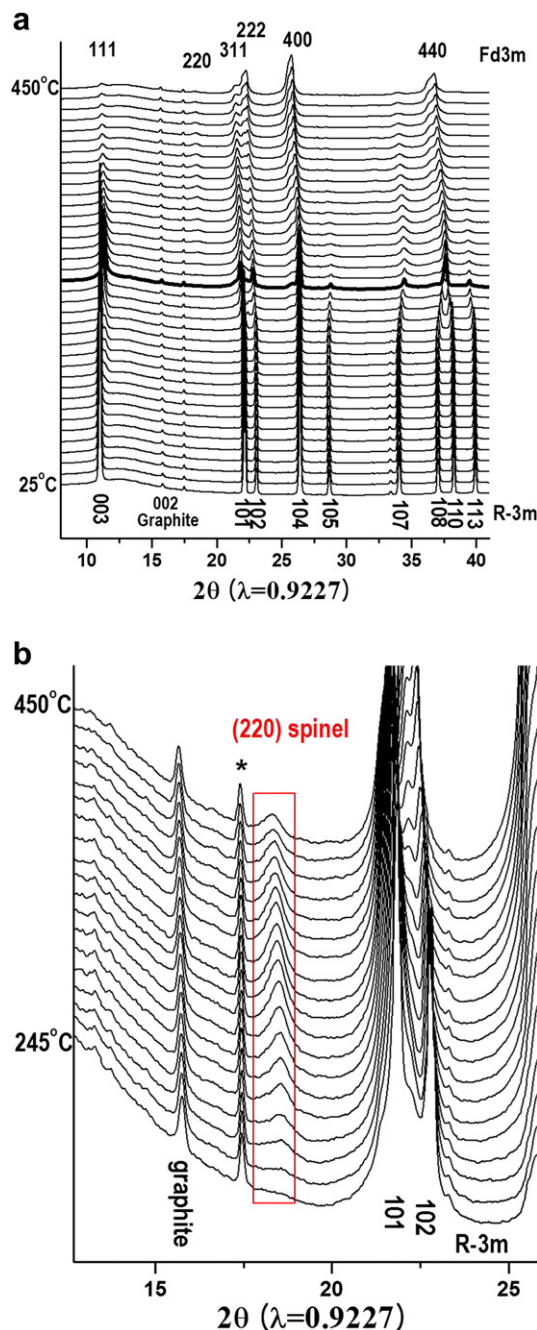


Fig. 6. (a) Time-resolved XRD patterns for MgO-coated  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte as a function of temperature. Formation of spinel phase starts at ~245 °C (thick line). Asterisk shows formation of metallic nickel phase. (b) Magnified XRD patterns in the temperature range between 245 and 450 °C in (a). Empty rectangular shows formation of spinel phase.

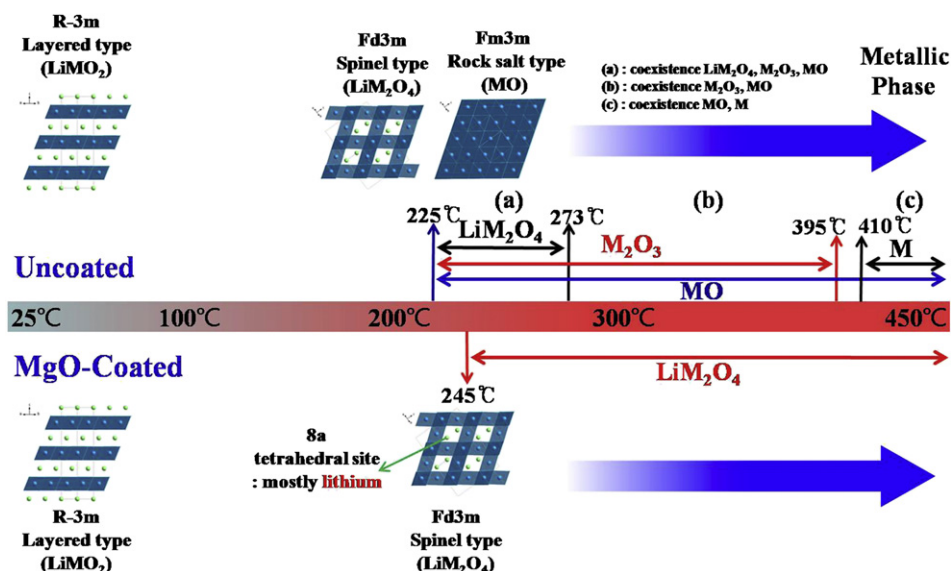


Fig. 7. Schematic illustration of crystal structural changes of the uncoated and MgO-coated  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte heated from 25 to 460 °C.

that the majority of the original layered structure is preserved in Fig. 5, even when heated to 450 °C at the end of heating. The in situ XRD of MgO-coated sample showed significant suppression of thermal decomposition reaction. This suggests that the interfacial reaction between the electrolyte and the cathode is a critical factor for the exothermic thermal decomposition reaction. When the surface of the cathode material is isolated from the electrolyte by the MgO surface coating, the accelerating effects of the electrolyte are significantly suppressed.

In situ XRD patterns during heating from 25 to 450 °C for the MgO-coated  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  (high state of charge) in the presence of electrolyte are plotted in Fig. 6. Similar like the XRD results of uncoated samples with various Li contents shown in Figs. 2 and 4, the thermal stability of the MgO-coated  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  (high state of charge) electrode decreases with decreasing lithium content in Fig. 6, in comparison with that for the  $\text{Li}_{0.67}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  (low state of charge) in Fig. 5. On the other hand, it is quite interesting to see that no NiO phase can be observed during the whole temperature range up to 450 °C for the MgO-coated sample in Fig. 6. The improved thermal stability of the MgO-coated cathode material at highly charged state is clearly demonstrated by the suppression of the formation of NiO structure. In the interval between 220 and 270 °C the coalescence of the (108) and (110) peaks in the layered structure is observed suggesting the formation of disordered spinel phase. Based on a  $2 \times 2 \times 2$  cubic rock salt unit cell, this merged peak corresponds to the (440) peak in the cubic structure with space group Fd3m [18,19]. The evolution of the (220) diffraction line also confirms the formation of the spinel phase [9]. At temperatures above 245 °C, a cubic structure is observed, consistent with the formation of  $\text{LiNi}_2\text{O}_4$ -like phase. The disordered spinel phase remains mostly unchanged until 450 °C. In comparison of the thermal behavior of MgO-coated electrode in the presence of electrolyte with the uncoated electrode in the absence of electrolyte, it is notable that the thermal behavior of surface-coated sample in the presence of electrolyte is very similar to that of the uncoated sample at the same charged state without electrolyte. This gives a strong experimental support to the thermal decomposition mechanism we propose: the thermal decomposition of nickel-based cathode is triggered and accelerated by the interaction between the surface of the cathode and the electrolyte and it can be suppressed by oxide coating (for example MgO coating) on the surface of the cathode materials.

Fig. 7 shows schematic illustration of crystal structural changes of the uncoated and MgO-coated  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte heated from 25 to 450 °C. The MgO-coated  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte shows higher beginning and ending temperature of the phase transition from layered to the spinel-type phases than those of the uncoated  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  indicating better thermal stability. Since the interaction between the surface of the charged electrode and the electrolyte plays a critical role on the thermal decomposition reaction of the charged electrode, surface modification such as metal oxide coating can significantly improve the thermal stability of the charged electrode.

#### 4. Conclusion

In situ XRD analysis has been carried out to investigate the thermal decomposition reaction of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  and MgO-coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte during heating from 25 to 450 °C. The electrolyte accelerates the thermal decomposition of the charged cathode material. The presence of the electrolyte alters the paths of the structural changes and lowers the onset temperatures of the reactions. As the degree of Li-ion deintercalation increases, the thermal decomposition takes place at less elevated temperature. At low states of charge ( $x < 0.5$ ) the reaction of  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  with the electrolyte at elevated temperature forms NiO and  $\text{Li}_2\text{CO}_3$ . The solvent acts as a reducing agent, and also lithium extracted from the structure reacts with the solvent resulting in the formation of  $\text{Li}_2\text{CO}_3$ . In situ XRD results for  $\text{Li}_{0.33}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  (high states of charge with  $x > 0.5$ ) in the absence of electrolyte during heating from 25 to 450 °C, show that the original layered structure converts to a disordered spinel structure first, then the disordered spinel structure converts to a NiO-like rock salt structure at higher temperature. For this high state of charge sample in the presence of electrolyte, the NiO-like phase starts its formation at the temperature as low as ~225 °C, together with the intermediate phase  $\text{Ni}_2\text{O}_3$ . This electrolyte induced thermal decomposition can be successfully suppressed by MgO surface coating. From the in situ XRD results for MgO-coated  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in the presence of electrolyte, at both low and high state of charge in the presence of electrolyte, the formation for both  $\text{Li}_2\text{CO}_3$  in low state of charge and  $\text{Ni}_2\text{O}_3$  in high state of charge

are totally suppressed. More interestingly, the formation of NiO-like rock salt structure is completely suppressed when heated to a temperature as high as 450 °C. These results confirmed the thermal decomposition mechanism we proposed: the thermal decomposition of nickel-based cathode is triggered and accelerated by the interaction between the surface of the cathode and the electrolyte and it can be suppressed by oxide coating (for example MgO coating) on the surface of the cathode materials.

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